Nonlinear Magneto-Optical Response from Quantum Well States in Noble Metals: Double Period and Interface Localization

A. Kirilyuk and Th. Rasing
Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

R. Mégy and P. Beauvillain
Institut d'Electronique Foundamentale, Université Paris-Sud, 91405 Orsay Cédex, France

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The nonlinear optical response from quantum well states in ultrathin noble metal films is shown to dominate the total generated second harmonic output from such films. The observed oscillatory behavior with overlayer thickness shows a period doubling with respect to that observed in linear Kerr measurements. This is shown to be related to the symmetry properties and interface localization of the quantum well states. [S0031-9007(96)01733-4]

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One of the most fascinating observations in magnetic multilayer studies of recent years is the formation of quantum well states (QWS) in ultrathin films [1]. Such QWS in a nonmagnetic spacer sandwiched in between two ferromagnetic layers may act as the mediator for the oscillatory exchange coupling and giant magneto resistance.

QWS were observed, e.g., in direct and inverse photoemission experiments [1–4]. However, the most widely used technique for the study of thin film magnetic properties is the magneto-optical Kerr effect (MOKE). Very recently MOKE has been used to study QWS in the Fe/Au(001) system [5]. The observed periods of the oscillatory dependence of the Kerr angle as a function of iron thickness could be related to the band structure of iron [5,6]. In contrast, in another studied system—Au(111)/Co(0001)—the observed oscillations of the Kerr rotation [7] could not be related to any spanning vector of the (constructed) Fermi surface. MOKE studies of QWS are complicated by the fact that the QWS-induced Kerr angle oscillations are a very small part of the already quite low total MOKE signal. That is why the linear optical measurements are difficult and often ambiguous.

Magnetization induced second harmonic generation (MSHG) is a nonlinear version of the MOKE technique [8–12]. Recently, it has been demonstrated to have at least two major advantages: an enhanced sensitivity to very narrow film interface regions [10,11] and a very large magneto-optical response [12]. Considering the recent calculations predicting a possible interface localization of the QWS-induced density of states [13] and the enhanced **k**-space selectivity [14], MSHG can be expected to be a powerful tool in studying the properties of such QWS. In addition, the three-photon nature of MSHG could give rise to new (compared with MOKE) oscillatory periods appearing as a function of the film thickness [14].

In this Letter we demonstrate that the nonlinear magneto-optical response from thin wedge-shaped noble metal overlayers on various magnetic substrates is strongly influenced by QWS, in agreement with the interface sensitivity of MSHG plus the predicted QWS interface localization. For all studied samples, the observed oscillatory behavior of the MSHG signals reveals a period which is approximately *twice* the period observed with linear MOKE. This can be explained by a simple model taking into account the symmetry of the QWS wave functions and is in good agreement with a multiple scattering analysis of the experimental data.

The second harmonic polarization $\mathbf{P}(2\omega)$ of a magnetic medium is generally described by a third rank polar tensor χ_{ijk}^{cr} for the crystallographic contribution and a fourth rank axial tensor $\chi_{ijkl}^{\mathrm{magn}}$ for the magnetization-induced part:

$$P_i(2\omega) = \chi_{ijk}^{\mathrm{cr}} E_j(\omega) E_k(\omega) + \chi_{ijkl}^{\mathrm{magn}} E_j(\omega) E_k(\omega) M_l \,, \tag{1}$$

where $\mathbf{E}(\omega)$ is the incoming light field and $\mathbf{M}$ is the magnetization of the medium. In centrosymmetric materials, both tensors are nonzero only at surfaces and interfaces, where the inversion symmetry is broken. For a particular magneto-optical configuration, e.g., polar or transversal (and for a high-symmetry surface), one may consider only one simplified third rank tensor with different components that are either even in $\mathbf{M}$, describing the crystallographic part, or odd and thus relate to the magnetization-induced contribution [8]. Equation (1) is then written as

$$\mathbf{P}(2\omega, \pm\mathbf{M}) = [\vec{\chi}_{\mathrm{even}}(\pm\mathbf{M}) \pm \vec{\chi}_{\mathrm{odd}}(\pm\mathbf{M})] E^2(\omega) \,, \tag{2}$$

where $\vec{\chi}_{\mathrm{even}}$ and $\vec{\chi}_{\mathrm{odd}}$ are linear combinations of, respectively, even and odd tensor elements. In the polar geometry, $\vec{\chi}_{\mathrm{even}}$ and $\vec{\chi}_{\mathrm{odd}}$ are orthogonal to each other so the vector sum within the brackets results in a second harmonic (SH) polarization plane rotation of $\alpha \approx \frac{|\chi_{\mathrm{odd}}|}{|\chi_{\mathrm{even}}|}$. In the transversal geometry, in contrast, both $\vec{\chi}_{\mathrm{even}}$ and $\vec{\chi}_{\mathrm{odd}}$

act along the same direction, and Eq. (2) shows then a change in the absolute value of $\mathbf{P}(2\omega)$, i.e., a change in the SH intensity $I_{\mathrm{SH}} \propto |P(2\omega)|^2$. Then, the magnetization contrast can be defined as

$$\rho = \frac{I(+\mathbf{M}) - I(-\mathbf{M})}{I(+\mathbf{M}) + I(-\mathbf{M})}, \tag{3}$$

where $I(\pm\mathbf{M})$ are the SH intensities measured for opposite directions of the sample magnetization. Here, in contrast with MOKE, the average intensity I_{SH} is also an important parameter directly representing the electronic structure of an interface or a thin film.

Our samples were step-shaped wedges of Au(111) or Cu(111) epitaxially grown on top of thin (5–20 ML) Co(0001) films on a Au(111) substrate. The copper wedge was covered by 10 ML of gold for protection. The Co films were also grown as steps, with a few different thicknesses. Because of the strong interface-induced perpendicular magnetic anisotropy in this system, we had the possibility to use different (polar or transversal) magneto-optical configurations, depending on the Co thickness.

For the MSHG measurements, a pulsed laser beam from a Ti-sapphire laser (82 MHz × 100 fs pulses) was focused onto the sample, while the latter could be moved with the help of a stepping motor in a magnetic field either in plane or perpendicular to the sample. After proper filtering, the outcoming specular SH light was detected with a photomultiplier. In the polar configuration, the Kerr rotation of the SH polarization was measured similar to what has been described in Ref. [12]. In the transversal configuration, we checked that for both P_{in} and S_{in} incoming light polarizations, the SH output was always strictly P polarized (P_{out}), in agreement with theory [8]. As a magnetic signal, we measured the magnetic contrast ρ [Eq. (3)].

Figure 1(a) shows that the generated total SH intensity exhibits a strongly oscillatory behavior as a function of the gold overlayer thickness that can be very well described by damped cosines. The slight change of the observed periods for the curves measured with 720 and 850 nm wavelengths appeared not to be significant: we checked that in the region of 720–1170 nm the period is constant ($\Lambda \approx 13$–14 ML) within 10%–15% [see inset in Fig. 1(a)].

The same kind of oscillatory behavior has also been found for the magnetization dependent SHG. Figure 1(b) shows the relative magnetic signal ρ for a 20 ML thick Co layer, while the SH polarization rotation is plotted in the inset for the perpendicularly magnetized 6 ML Co film. All the observed periods are basically the same as given above for the intensities. However, the shape of these curves is more complicated than simple damped oscillations. This is due to the fact that the magnetic signals are calculated as a ratio of different oscillatory terms [e.g., Eq. (3)]. This may explain why the doubled period (see below) was not discovered in Ref. [10] where only magnetic signals were considered, while SH intensity data of Ref. [15] clearly show the long period oscillations.

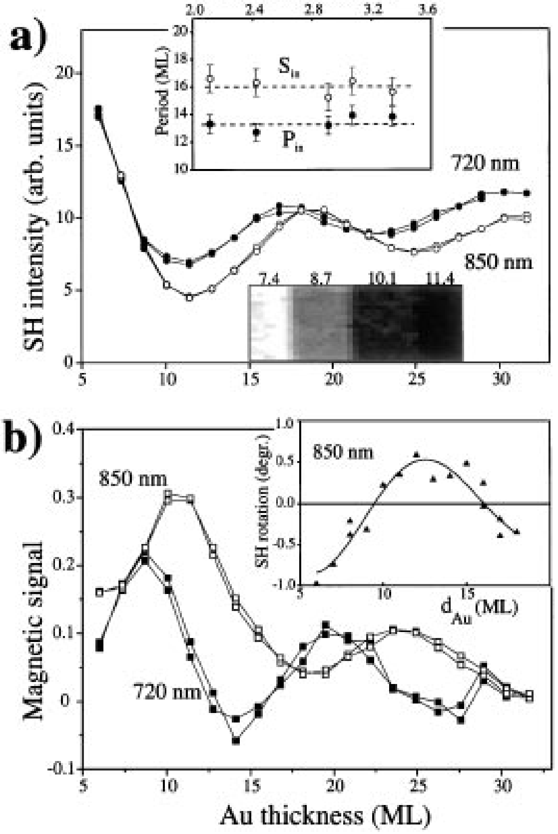

FIG. 1. (a) SH intensity ($P_{\mathrm{in}}P_{\mathrm{out}}$ polarization combination) as a function of the Au(111) overlayer thickness on a 20 ML thick Co film. Gray-scale SH image of the part of the sample shows a very strong thickness dependence of MSHG as well as a perfect homogeneity of the sample. Inset shows a photon energy dependence of the oscillation periods for $P_{\mathrm{in}}P_{\mathrm{out}}$ and $S_{\mathrm{in}}P_{\mathrm{out}}$ polarization combinations. (b) Relative magnetic signal and SH polarization rotation (in inset) as a function of the gold thickness.

A linear MOKE study performed on the same kind of samples [7] reported oscillations of the Kerr rotation with the much shorter period of 7.7 ML. This strong difference with our results might be assigned to the different wavelength region used for the MOKE experiments (540–630 nm). To fill the gap, we did MOKE measurement using the same Ti-sapphire laser at $\lambda = 850$ nm. This resulted in a period of 7 ± 1 ML. That is, in the case of $\lambda_{\mathrm{MOKE}} = \lambda_{\mathrm{SH}}$, the total excitation energy was equal for the two experiments. We also investigated the situation $2\lambda_{\mathrm{MOKE}} = \lambda_{\mathrm{SH}}$ to study possible effects of initial and intermediate or intermediate and final states. However, again the observed MSHG period was always *twice* as large as the period detected with MOKE. Hence the difference in periods cannot be explained by the different total excitation energy ($\hbar\omega$ versus $2\hbar\omega$).

It has been already discussed [10–12] that for a thin film the corresponding tensor elements on the opposite film interfaces are related to each other by a mirror symmetry and therefore they differ only by a phase factor of 180°. Hence the resulting total SHG signal arises from the competition between the signals from the two film interfaces that mostly cancel each other and only depends on the difference in their local fields. In other words, the nonlinear polarization $\mathbf{P}(2\omega)$ is an *odd* function with respect to the film symmetry plane.

Within this approach, the influence of QWS on MSHG would be largely canceled too because every QWS contributes symmetrically (via its local density of states) to the χ tensor elements of both interfaces. Even for the nonsymmetric geometry (like our case—Co/Au and Au/air interfaces) one may still argue that the corresponding electron wave functions are rather symmetric once they form a confined state.

Following these arguments, *one may expect no QWS effects on the MSHG signal at all.* This is contrary to the experimental observations of a total domination of QWS on the SHG response. That we do observe a (rather strong) signal is partly related to the fact that the local electromagnetic fields at the two interfaces are different (this follows from Fresnel formulas) and partly from the (*a*-) symmetry of the QWS wave functions. In a simple textbook picture the confined QWS have alternating odd and even character; i.e., the asymmetry of the QWS wave functions is repeated with the double period. This asymmetry can be expressed as a relative phase factor between the two QWS interface contributions (the Co/Au and the Au/air). Because the total SHG response results from a *coherent* superposition of these interface contributions, this total response will also display a periodic behavior with the double period, despite the fact that the individual contributions oscillate with the single period. Because the linear MOKE experiment probes only the Co/Au region, MOKE indeed shows the single period. We emphasize that it is the wave function phase at a given interface which plays a crucial role and, without interference, the effect would be unobservable. We also stress that the thickness dependence of the local fields can be neglected for these ultrathin films.

To test these ideas, we decomposed the total MSHG signal into the contributions from different interfaces. This is possible using a transfer matrix technique (as described in Ref. [16]) once enough independent experimental data are available. For this purpose, first the angle-of-incidence dependencies of the MSHG signals were measured for each gold overlayer thickness value (see Fig. 2). Next, a fit of these data was performed, using the χ tensor elements as fitting parameters. For the fit to be unique, one has to use either $S_{\mathrm{in}}P_{\mathrm{out}}$ or $Q_{\mathrm{in}}S_{\mathrm{out}}$ (Q is the polarization in between P and S) polarization combinations. In both cases, there is only one even (and one odd) χ component per (magnetic) interface. The results of the calculations may be summarized as follows.

(i) There is a small bulk contribution which is thickness independent. In Fig. 2 this contribution produces a discrepancy between the fitting curves (which take into account the interface contributions only) and the experimental data in the region of 30°–50°. To include this feature in the fit, one has to assume bulk electric quadrupole contributions of the type $\chi^{(Q)}_{ijkl}E_j\nabla_k E_l$, where components of the type $zyzy$, $xyxy$, etc., are nonzero also in centrosymmetric media.

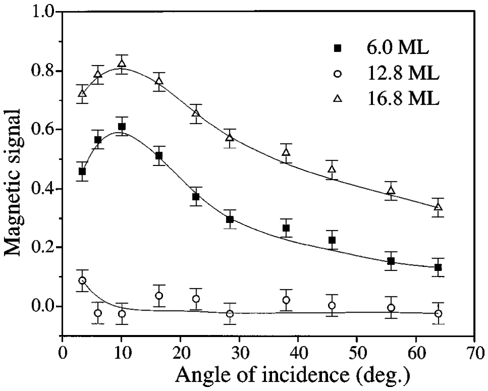

FIG. 2. Relative magnetic signal as a function of the angle of incidence for three different gold thicknesses (indicated in the figure) and for the $S_{\mathrm{in}}P_{\mathrm{out}}$ polarization combination. Solid lines are theoretical fits taking into account only the interface contributions.

(ii) The major part of the signals can very well be described with a model taking into account only the interface MSHG (Fig. 2). Oscillatory behavior of the signals naturally originates from the corresponding behavior of the tensor components. Figure 3(a) shows the individual χ components of the two gold layer interfaces as a function of the film thickness, displaying an oscillatory behavior with a mean period of around 6–8 ML, i.e., the same period as observed by MOKE. However the resulting SHG intensity and magnetic signal perfectly fit the experimentally observed slowly oscillating behavior with the double period [see Fig. 3(b)]. This means that while the local density of states and hence the χ tensor at each interface show the standard QWS period, the resulting total response includes also the phase between the corresponding elements and therefore allows a slower variation. This is possible, of course, only because the interfaces are not independent as soon as every QWS wave function is located at both interfaces simultaneously. Although it is not exactly correct to talk about "contributions of different interfaces" in such conditions, it is still possible to formally use this model. One should mention here that the χ components of different interfaces may be determined accurately only relative to each other. Their absolute values, on the contrary, may contain rather large systematic errors. However, the derived fast-oscillatory behavior of the χ tensor is obtained from the best fit of the (slowly oscillating) experimental data, and may be considered as a strong support of our model.

As for the linear MOKE technique, although it has "bulk" sensitivity, the oscillatory part of the signal is

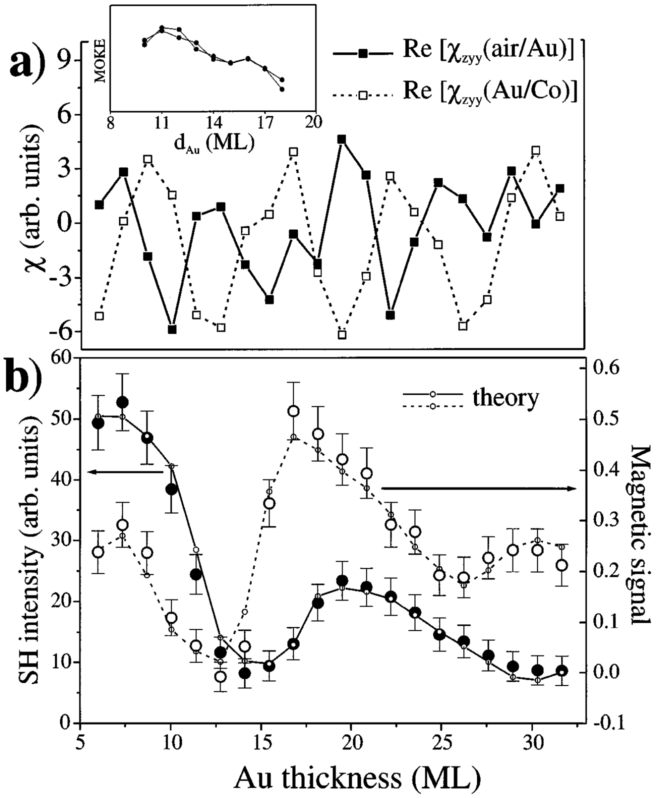

FIG. 3. (a) Tensor components of different Au(111) film interfaces as a function of the film thickness. Inset shows the Kerr ellipticity as a function of gold thickness. Visible oscillations have a period of about 7 ML which is roughly equal to that for the tensor components. (b) Theoretical fit of the SH intensity (solid dots) and relative magnetic signal (open dots) using the parameters shown in (a).

provided by the narrow region along the Au/Co interface, where spin polarization of electrons is affected the most. Therefore it is related to the local density of states at this interface only, which oscillates with a single QWS period.

Although not shown here, very similar results were obtained for the Cu(111) overlayer, with corresponding periods of 12–14 ML. The main difference was the observed amplitude of the intensity oscillations which was much smaller than for Au(111). The recently detected linear MOKE oscillations on such kinds of samples [17] showed a period of 7 ML. Hence, the period doubling is confirmed also for another system.

In conclusion, we have shown that the new nonlinear magneto-optical technique MSHG has an extremely high sensitivity for the appearance of QWS in ultrathin metallic films. It is not only possible to detect the QWS in noble metals through their influence on the magnetic substrate (like linear MOKE does), but to study the nonmagnetic part directly as well. The discovered small nonoscillatory bulk contribution to MSHG strongly supports the idea of the interface localization of QWS. But the most interesting discovery is that while the bulk inversion symmetry of a medium leads to the interface selectivity of MSHG, the symmetry of the quantum well states in an ultrathin film additionally restricts the MSHG process. As a consequence, MSHG signals oscillate as a function of the film thickness with a period doubled in comparison to that measured with linear MOKE. The small difference in periods for the two incoming light polarizations may be only tentatively explained by the fact that different χ elements depend on different electronic states in a metal [18]. To further develop this subject, theoretical calculations are very desirable, taking into account realistic eigenfunctions of a thin metal film forming a quantum well. From the experimental point of view, it would be very interesting to study also a *magnetic* thin film as well as to increase the spectral region of measurements.

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